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## Description

This invention relates to electrically conducting materials and a process for the preparation of such electrically conducting materials.

5 Numerous methods for imparting electrical conductivity to synthetic polymeric materials in the form of a shaped body are known in the art. For example, in United States patent No. 3,940,533, there is proposed a method for imparting electrical conductivity to polymeric shaped materials such as polyamide fibres, in which the fibres are first contacted with hydrogen sulphide and the resulting fibres having the hydrogen sulphide impregnated therewithin are then immersed in a metal salt solution such as an aqueous copper sulphate solution, to form a deposit of metal sulphide, such as copper sulphide, on the fibres. This process, 10 however, is not applicable to acrylic fibres. Moreover, the copper sulphide-deposited fibres obtained according to this process is poor in stability, especially in washability, so that the electrical conductivity gradually decreases during use. In United States patent No. 4,336,028 (EP—A1—0035406), there is disclosed a method for imparting electrical conductivity to acrylic fibres by impregnating the fibres with copper sulphide. Although the electrically conducting fibres obtained by this method can exhibit far 15 superior washability in comparison with those obtained according to the method of the abovementioned United States patent No. 3,940,533, the washability is still desired to be improved in practice.

In accordance with the present invention there is provided an electrically conducting material comprising a cyano group-containing material having adsorbed thereby sulphides of copper and at least 20 one auxiliary metal selected from the group consisting of silver, gold and elements of the platinum group.

In another aspect of the present invention, there is provided a process for the preparation of an electrically conducting material, comprising treating a cyano group-containing material with (a) a source of monovalent copper ions, (b) a source of ions containing an auxiliary metal selected from the group consisting of silver, gold and elements of the platinum group and (c) a sulphur-containing compound to 25 adsorb sulphides of copper and the auxiliary metal by the cyano group-containing material.

In a still further aspect, the present invention provides a method of improving the stability of an electrically conducting, copper sulphide-carrying, cyano group-containing material, comprising treating said cyano group-containing material with a source of ions containing an auxiliary metal selected from the group consisting of silver, gold and elements of the platinum group.

30 The cyano group-containing material to which electrical conductivity is to be imparted includes both polymeric substances and water-insoluble low molecular substances having one or more cyano groups. The cyano group-containing polymeric substances involve both natural and synthetic polymers.

Not only acrylonitrile-series polymeric substances such as polymers and copolymers (inclusive random, block and graft copolymers) of acrylonitrile but also other polymeric substances such as 35 polyamides and polyesters having introduced therein cyano groups may be used as the synthetic polymers. The introduction of cyano radicals into such synthetic polymers may be done by any known methods such as by reaction with dicyandiamide, graft polymerization of acrylonitrile onto the polymers, cyanoethylation, mixed spinning, graft polymerized material spinning, blocked polymerized material spinning and the like. The synthetic polymers to be imparted with electrical conductivity may be in the form 40 of powder or in the form of a shaped body such as a film, plate, fibre, fabric, paper, sheet, block, pellet, string, thread, rod or pipe and can contain customarily used additives such as an ultraviolet ray-absorber and a molding aid.

The cyano group-containing natural polymeric materials include polypeptides and polysaccharides, such as wool, silk and cotton, having introduced therein cyano radicals. The introduction of cyano 45 radicals into such naturally occurring polymeric materials may be done in any known way such as exemplified above. The cyano group-containing natural polymers may be used in the form of powder or fibres.

Illustrative of the cyano group-containing water-insoluble low molecular compounds are phthalonitrile, isophthalonitrile, N-cyano-methylaniline and N-β-cyanoethylaniline. These compounds are 50 generally used in the form of powder.

In the process of the invention, the cyano group-containing material is subjected to a treatment with (a) a source of monovalent copper ions (b) a source of ions containing an auxiliary metal selected from the group consisting of silver, gold and elements of the platinum group and (c) a sulfur-containing compound to form sulphides of copper and the auxiliary metal adsorbed on and/or within the cyano group-containing 55 material. The platinum group elements herein include ruthenium, rhodium, palladium, osmium, iridium and platinum.

As the source of monovalent copper ions, a combination of a bivalent copper compound, such as a salt or a complex of bivalent copper, and a reducing agent capable of converting the bivalent copper compound into monovalent copper ions is generally employed. Illustrative of the bivalent copper salts are cupric sulphate, cupric chloride, cupric nitrate and cupric acetate. Examples of the reducing agent include metallic 60 copper, hydroxylamine or its salt, ferrous sulphate, ammonium vanadate, furfural, sodium hypophosphite and glucose. Cuprous salts or complexes may also be used as the source of monovalent copper ions.

The sulphur-containing compound used in the process of this invention is of a type which is capable of 65 providing sulphur atoms and/or sulphur ions for reaction with the copper ions and the ions containing the auxiliary metal to form sulphides of copper and the auxiliary metal which are adsorbed on or within the

cyano group-containing material. Illustrative of the sulphur-containing materials are sodium sulphide, sulphur dioxide, sodium hydrogen sulphite, sodium pyrosulphite, sulphurous acid, dithionous acid, sodium dithionite, sodium thiosulphate, thiourea dioxide, hydrogen sulphide, sodium formaldehyde sulphonylate (rongalite C), zinc formaldehyde sulphonylate (rongalite Z) and mixtures thereof. Since these sulphur-containing compounds have a reducing activity, they may be used as at least a part of the reducing agent for converting bivalent copper ions into monovalent ones.

As the source of ions containing the auxiliary metal, a salt or complex of the auxiliary metal, such as a sulphate, nitrate, chloride, acetate, benzoate, a thiocyanate complex or a thiosulphate complex, may be suitably employed.

The treatment with the components (a), (b) and (c) may be effected in the order of (I): (a) (b) (c), (a) (b)-(c), (a)-(b) (c), (a)-(b)-(c) and (b)-(a)-(c); and (II): (a)-(c)-(b)-(c), (a)-(c)-(b), (a)-(c)-(b) (c), (a) (c)-(b) (c), (a) (c)-(b), (a) (c)-(b)-(c). The methods of group (I) form sulphides of copper and the auxiliary metal simultaneously while the methods of group (II) form copper sulphide prior to the modification by the auxiliary metal component.

Among the group (I) methods, the first three are preferred from the economic point of view, i.e. it is preferable to conduct the treatment with the source of ions containing the auxiliary metal simultaneously with at least one of the treatments with the source of monovalent copper ions and sulphur-containing compound. When the treatments with the source of monovalent copper ions and the source of ions containing the auxiliary metal, and with the sulphur-containing compound are simultaneous ((a) (b) (c)), the cyano group-containing material to be treated is immersed in a bath containing the source of monovalent copper ions, the source of ions containing the auxiliary metal and the sulphur-containing compound preferably at a temperature of 20 to 150°C, more preferably 30 to 100°C for a period of time of generally 1 to 24 hours. When the reaction is conducted at an elevated temperature, it is preferred that the bath be gradually heated at a rate of 1 to 3°C/min. The pH of the bath is preferably controlled to be in the range of about 1.5 to 6, more preferably 3 to 5. For this purpose, a pH controlling agent may be used. Examples of the pH controlling agent include inorganic acids such as sulphuric acid, hydrochloric acid and phosphoric acid; organic acids such as citric acid and acetic acid; and mixtures thereof. It is possible to carry out the treatment at a low temperature when the pH is low.

In the embodiment of the present invention wherein the treatment with the sulphur-containing compound is preceded by the treatment with the source of monovalent copper ions and the source of ions containing the auxiliary metal ((a) (b)-(c)), the cyano group-containing material is first immersed in a first bath containing the source of monovalent copper ions and the source of ions containing the auxiliary metal, preferably at a temperature of 50 to 150°C, more preferably 80 to 110°C, for a period of time so that monovalent copper ions and ions containing the auxiliary metal are adsorbed by the cyano group-containing material (first stage). The reaction time is generally 0.5 to 2 hours. The pH of the first bath is preferably controlled in the range of 1 to 3 with the use of such a pH controlling agent as described above. As described previously, the treatment with monovalent copper ions may also be conducted prior to or after the treatment with the auxiliary metal-containing ions ((a)-(b)-(c) or (b)-(a)-(c)). In such a case, the conditions of the treatment are substantially the same as those described immediately above. However, such a method does not afford any specific advantage over the method in which the component (a) is used together with the component (b). The cyano group-containing material from the first stage having the adsorbed monovalent copper ions and ions containing the auxiliary metal is then treated in a second bath containing the sulphur-containing compound (second stage). Preferably, the treated material from the first stage is washed with a suitable liquid such as water prior to the second treatment stage. The treatment of the second stage is carried out preferably at a temperature of 50 to 120°C, more preferably 70 to 100°C. The reaction time generally ranges from 1.5 to 4.5 hours. It is preferable to gradually heat the bath at a rate of 1 to 3°C/min. In the case where the second stage employs a gaseous sulphur-containing compound, the treated material from the first stage is contacted therewith at a pressure of 0.5 to 3 atm. at a temperature of 90 to 120°C for 1 to 3 hours. In the case of a two stage method (a)-(b) (c), the reaction conditions are substantially the same as the previously described two stage method (a) (b)-(c).

In both the above single and two-stage treatments, the amount of the source of monovalent copper ions varies according to the intended degree of electrical conductivity, the content of cyano groups in the starting material, the form of the starting material and the like. Generally, the source of monovalent copper ions is used in an amount of 2 to 15 g in terms of metallic copper per 100 g of the starting cyano group-containing material. The concentration of the source of monovalent copper ions in the bath is generally 1 to 10 g/l in terms of elemental copper. The amount of the source of ions containing the auxiliary metal used is generally 0.001 to 0.5 mol, preferably 0.01 to 0.3 mol per mol of the monovalent copper ions. The amount of sulphur-containing compound is generally 1 to 3 mols per mol of the monovalent copper ions.

As described previously, the electrically conducting material of this invention may also be prepared by treating a cyano group-containing material having adsorbed thereby copper sulphide with a source of ions containing the auxiliary metal and, optionally, a sulphur-containing compound (Group II methods).

The copper sulphide-adsorbed, cyano group-containing material may be preferably prepared in accordance with the method described in United States patent No. 4,336,028 or Published, European patent application EP—A1—35406. Briefly, the method includes treating the above-mentioned cyano group-

containing material with (a) a source of monovalent copper ions of a type as described previously and (c) a sulphur-containing compound of a type as described previously. The treatment with the sulphur-containing compound is simultaneous with or preceded by the treatment with the source of monovalent copper ions.

5 The resultant material having adsorbed thereby copper sulphide ( $\text{Cu}_x\text{S}$  where  $x$  is in the range from 1 to 2 such as covellite ( $\text{CuS}$ ), digenite ( $\text{Cu}_{1.8}\text{S}$ ) or chalcocite ( $\text{Cu}_2\text{S}$ )) is then treated, as such or after being washed with water, in a bath containing the above mentioned source of ions containing the auxiliary metal. The concentration of the auxiliary metal-containing ions in the bath is generally in the range of 0.005—10 g/l, preferably 0.01—6 g/l in terms of the elemental metal. The treatment is performed at a temperature  
10 from room temperature to  $100^\circ\text{C}$ , preferably  $30$ — $80^\circ\text{C}$ , for a period of 0.5—20 hours, preferably 1—10 hours with a ratio by weight of the bath to the material to be treated being in the range of 5:1 to 50:1, preferably 10:1 to 30:1.

It is preferred that the treatment with the auxiliary metal-containing ions be performed in the presence of the above-mentioned sulphur-containing compound or be followed by the treatment with the sulphur-containing compound to further improve both the stability and the electrical conductivity of the  
15 resulting electrically conducting material. The sulphur-containing compound is generally used in an amount of 0.2—5 mols, preferably 0.4—3 mols per mol of the source of auxiliary metal-containing ions.

As a result of the foregoing treatments, sulphides of copper and the auxiliary metal are adsorbed by the cyano group-containing material to form a continuous, electrically conducting layer or deposit at least  
20 on the surface thereof. The X-ray diffraction pattern of the electrically conducting material of this invention in which silver is used as the auxiliary metal has been found not to be the same as that deduced from the X-ray diffraction patterns of copper sulphide and silver sulphide. The analysis of the electrically conducting material by an X-ray microanalyzer indicates that the silver exists at the same locations as the copper and sulphur. Further, in view of the fact that the electrically conducting material of this invention shows a  
25 property which is not expected from the properties of a cyano group-containing material having either copper sulphide or the sulphide of the auxiliary metal, the electrically conducting layer is not considered to be formed of a mere mixture of copper sulphide and the sulphide of the auxiliary metal. Rather, it is believed that at least some of the copper sulphide and the auxiliary metal sulphide are present in a mixed crystal-like form in which the auxiliary metal is associated with the sulphur atom or atoms of the copper  
30 sulphide.

The amount of copper sulphide adsorbed by the cyano group-containing material varies depending on the kind of the starting cyano group-containing material and the intended electrical conductivity but is generally in the range of about 0.5 to 30%, preferably 1 to 15%, in terms of elemental copper based on the weight of the starting cyano group-containing material.

35 The amount of the sulphide of the auxiliary metal in the electrically conducting material of this invention can be sufficiently low and is, in general, such that the atomic ratio  $M/\text{Cu}$ , where  $M$  stands for the auxiliary metal, is 0.0001 to 0.5, preferably 0.001—0.3, more preferably 0.01—0.2. Too small an amount of the auxiliary metal component is insufficient to attain an improvement in washability, whereas an amount of the auxiliary metal component in excess of 0.5 of the  $M/\text{Cu}$  atomic ratio tends to lower the electrical conductivity and is also disadvantageous from the economic point of view since the auxiliary metal is very  
40 expensive.

In addition to the above-described auxiliary metal, iron, cobalt or nickel has been found to be effective in lightening the color of the electrically conducting material. Such a second metal component may be incorporated into the electrically conducting material in the same manner as the auxiliary metal  
45 component. Thus, a source of ions containing the second metal, such as a salt or complex thereof is added to the bath which is used for treating the cyano group-containing material with the source of monovalent copper ion, the source of ions containing the auxiliary metal and/or the sulphur-containing compound. If desired, the incorporation of the second metal component can be done independently of the above treatments by treating the cyano group-containing material in the same manner and conditions as in the  
50 case of the treatment with the source of ions containing the auxiliary metal. The amount of second metal-containing ions used in either case of treatment is generally 0.01 to 0.5 mol per mol of the monovalent copper ions.

The electrically conducting material of this invention, when in the form of fibres, may be advantageously utilized as clothes, carpets, interior decorative sheets, gloves or like by themselves or in  
55 combination with other fibres because of their freedom of static charging and easiness to be dyed. When in the form of a film or plate, the electrical conductivity and transparency of the materials of this invention allow the use thereof as a cover or enclosure for electric parts such as integrated circuits and large-scale integrated circuits which are required to be shielded from electrostatic charges during storage or transportation. The powdery, electrically conductive material of this invention may be incorporated into a  
60 coating composition to form electrically conductive coatings. Because of the excellent thermal stability of the sulphides, the powdery or granular, electrically conductive material of this invention formed from synthetic polymers, such as polyacrylonitrile, can be subjected to thermal molding conditions to produce electrically conducting molded articles. Thus, the electrically conducting materials of this invention lend themselves to numerous applications in many fields.

65 The following examples will further illustrate the present invention. In the examples, the washability

was determined according to the method speculated in Japanese Industrial Standard (JIS) L 1045. That is, a sample was added in a washing liquid containing 3 g/l of a commercially available detergent with a ratio by weight of the sample to the washing liquid of 1:50. The liquid was charged in a dye-fastness testing device together with ten stainless balls and agitated at 50°C for 30 min followed by washing with water and drying.

5 Such a procedure was repeated a number of times for the examination of the fastness to washing. The alkali spotting test was conducted in accordance with JIS L 0864. A sample (1 part by weight) was immersed in an aqueous solution (30 parts by weight) containing 10 g/l of sodium carbonate, which was refluxed for one hour.

#### 10 Example 1

5 g of an acrylic fibre CASHMILON (0.22 tex, 51 millimeters in length of cut, type FWBR) made by Asahi Chemical Industry Co., Ltd., Japan) were immersed in 100 ml of an aqueous bath containing 20 g/l of cupric sulphate, 6 g/l of silver sulphate, 20 g/l of sodium thiosulphate, 20 g/l of sodium hydrogen sulphite, 30 g of disodium hydrogen phosphate and 12 g of citric acid, and heat-treated therewithin at a temperature of 50°C for 5 hours. Subsequently, the fibre was thoroughly washed in water and dried to obtain a fibre having an electric resistivity of  $1.2 \times 10^{-1} \Omega\text{-cm}$ . The fibre withstood 100 times washing. For the purpose of comparison, the above procedure was repeated in the same manner as described except that no silver sulphate was used. The resulting electrically conducting fibre failed to show a practically acceptable electrical conductivity after 40 times washing.

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#### Example 2

5 g of polyacrylonitrile threads SILPALON (11.1 tex/40 filaments) Mitsubishi Rayon K.K.) were immersed in 100 ml of an aqueous bath containing 20 g/l of cupric sulphate, 3 g/l of nickel sulphate, 3 g/l of silver nitrate, 20 g/l of sodium thiosulphate, 10 g/l of sodium hydrogen sulphate, 30 g/l of disodium hydrogen phosphate and 12 g/l of citric acid, and heat-treated at 50°C for 3 hours. The resulting threads were thoroughly washed with water and dried to obtain light brown-gray threads having an electric resistivity of  $4.3 \times 10^{-1} \Omega\text{-cm}$ . The threads withstood 80 times washing. For the purpose of comparison, the above procedure was repeated in the same manner as described except that neither silver nitrate nor nickel sulphate was used. The resulting threads was unable to show a practically acceptable electrical conductivity after 40 times washing.

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#### Example 3

Example 1 was repeated in the same manner as described therein except that palladium chloride was used in place of silver sulphate. The resulting fibre had an electrical resistivity of  $3 \times 10^{-1} \Omega\text{-cm}$  and withstood 100 times washing.

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#### Example 4

A polyhexamethylene adipamide film BO#15, manufactured by Toray Co., Ltd.) having a thickness of 15  $\mu\text{m}$  and weighing 2.5 g was immersed in 200 ml of an aqueous solution containing 10 g/l of ammonium persulphate and 10 g/l of sodium hydrogen sulphite at room temperature for 30 min. for adsorbing the catalyzer. The thus treated film was then placed in a stainless steel vessel to which was charged acrylonitrile vapor for effecting graft copolymerization of acrylonitrile onto the film at 38—40°C for 3 hours. The film having cyano groups introduced thereinto was increased by 32.8% in weight. The resulting film was then immersed in a bath having the same composition as that of Example 1 for treatment at 50°C for 5 hours, thereby to obtain a transparent film having a surface resistivity of 180  $\Omega$ . The fastness to alkali spotting of the film was found to be improved by two grades (from rank 2 to rank 4) in comparison with the control nylon film obtained in the same manner as described above except that no silver sulphate was employed.

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#### 50 Example 5

A polyhexamethylene adipamide staple BO#15, manufactured by Toray Co., Ltd.) was immersed in an aqueous solution containing 5 g/l of ammonium persulphate and 5 g/l of sodium hydrogen sulphite at room temperature for 30 min. for adsorbing the catalyzer. The thus treated staple was then placed in a stainless steel vessel to which was charged acrylonitrile vapor for effecting graft copolymerization of acrylonitrile onto the film at 38—40°C for 3 hours. The staple having cyano groups introduced thereinto was increased by 25% in weight. 5 g of the resulting staple was then immersed in 100 ml of an aqueous bath containing 20 g/l of cupric sulphate, 3 g/l of ferrous sulphate, 4 g/l of silver nitrate, 20 g/l of sodium thiosulphate, 10 g/l of sodium hydrogen sulphite, 20 g/l of disodium hydrogen phosphate and 8 g/l of citric acid, and was heat-treated in the bath at 60°C for 3 hours to obtain an electrically conducting staple. The fastness of the staple to alkali spotting was found to be improved by two grades (from rank 2 to rank 4) in comparison with the control nylon staple obtained in the same manner as described above except that no silver nitrate was employed.

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#### Example 6

Polyacrylonitrile powder was ground to a particle size of 10  $\mu\text{m}$  or less and the ground powder was

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treated in the same manner as that in Example 1. The thus treated polyacrylonitrile powder was found to increase 12.0 wt% in weight. The electrically conducting powder was added into a vinyl chloride melt and the resulting melt, containing 5 wt% of the electrically conducting polyacrylonitrile, was then injected onto the surface of gloves formed of cotton. The gloves were effective in preventing problems caused by electrostatic charge.

#### Example 7

Phthalonitrile crystals were ground to a particle size of 10  $\mu\text{m}$  or less and 10 g of the ground phthalonitrile powder were treated in the same manner as that described in Example 1. The resulting powder was washed with water and dried to obtain about 11.1 g of electrically conducting phthalonitrile powder. The electrically conducting powder was then incorporated into a commercially available acrylic paint (Acrylite No. 500) with a mixing ratio by weight of 1:1. The resulting paint was coated on an iron plate. The coating was found to have a surface electrical resistivity of  $2 \times 10^2 \Omega$ . A radio wave was found to be attenuated by 25 dB upon reflection on the surface of the coated iron plate. The coated iron plate was usable as a material for absorbing electromagnetic waves.

#### Example 8

5 g of an acrylic fibre CASHMILON (0.22 tex, 51 millimeters in length of cut) made by Asahi Chemical Industry Co., Ltd., Japan) were immersed in 100 ml of an aqueous bath containing 30 g/l of cupric sulphate, 6 g/l of silver sulphate and 20 g/l of hydroxylamine sulphate. The bath was then heated from room temperature to 100°C and maintained at that temperature for 60 minutes. After being thoroughly washed with water, the fibre was immersed in 100 ml of another aqueous bath containing 12 g/l of sodium dithionite. The bath was then heated from room temperature to 80°C and maintained at that temperature for 3 hours. The electrically conducting fibre obtained after being thoroughly washed in water and dried had a light olive-brown color and an electrical resistivity of  $8 \times 10^{-2} \Omega\text{-cm}$ .

When this electrically conducting fibre was subjected to the repeated washing test, deterioration of its conductivity was hardly perceived even after 100 times washing.

#### Example 9

An acrylic fibre CASHMILON (0.22 tex, 51 millimeters in length of cut) made by Asahi Chemical Industry Co., Ltd., Japan) was immersed in an aqueous bath containing 20 g/l of cupric sulphate, 6 g/l of silver sulphate, 3 g/l of cobalt sulphate and 15 g/l of hydroxylamine sulphate. The bath was gradually heated from room temperature to 90°C and maintained at that temperature for 3 hours. After being washed with water, the resulting fibre was put into a closed receptacle having a gas inlet. Sulphur dioxide was fed into the receptacle until the pressure in the interior thereof reached 0.5 Kg/cm<sup>2</sup> gauge pressure. Then, saturated vapor at 105°C was fed into the receptacle until the pressure within the receptacle reached 1.0 Kg/cm<sup>2</sup> gauge pressure. After having shut the receptacle tightly, the fibre was allowed to react therein at 110°C for 90 min. It was taken out after cooling, washed thoroughly in water, and dried. The electrically conducting fibre thus obtained had a light olive-grey color. Its electrical resistivity was  $3.2 \times 10^{-1} \Omega\text{-cm}$ . The electrically conducting fibre was tested for washability and withstood 100 times washing. The above procedure was repeated using hydrogen sulphide in place of sulphur dioxide to obtain almost the same results as above.

#### Example 10

A copper sulphide-containing, electrically conducting fibre, obtained in accordance with the method described in Example 1 of United States patent No. 4,336,028, was immersed in an aqueous bath containing 5 wt% of silver nitrate, 15 wt% of sodium thiosulphate and 5 wt% of sodium sulphite with a ratio by weight of the fibre to the bath of 1:20, and heat-treated in the bath at 55°C for 2 hours. The thus treated fibre withstood 100 times washing while the non-treated electrically conducting fibre did not show practically acceptable electrical conductivity after 40 times washing.

The above procedure was repeated using  $\text{PdCl}_2$ ,  $\text{AuCl}_3$  and  $\text{PtCl}_4$  each in place of  $\text{AgNO}_3$ . The resulting fibre was found to be improved in washability.

#### Example 11

5 g of a textile formed of an acrylic fibre SILPALON (20 tex/60 filaments) is immersed in 100 ml of an aqueous bath containing 6 g/l of hydroxylamine chloride, 20 g/l of cupric sulphate and 1 g/l of palladium chloride and treated therein at 98°C for 1 hour. After being washed with water, the resulting textile is immersed in 100 ml of an aqueous solution containing 10 g/l of sodium thiosulphate for the treatment at 95°C for 2 hours. The thus treated textile was washed with water and dried to obtain an electrically conducting textile A having an electrical resistivity of  $2.1 \times 10^{-1} \Omega\text{-cm}$ . The washability test results of the textile A are shown in Table 1 together with, for the comparison purpose, those of the textile B obtained in the same manner as described above except that no palladium chloride was used.

TABLE 1

Sample	Number of washing operation					
	0	10	20	30	40	50
	Electrical resistivity ( $\Omega$ -cm)					
Textile A	$2.1 \times 10^{-1}$	$2.3 \times 10^{-1}$	$2.25 \times 10^{-1}$	$2.7 \times 10^{-1}$	$3.9 \times 10^{-1}$	$5.1 \times 10^{-1}$
Textile B	$1.8 \times 10^{-1}$	$1.86 \times 10^{-1}$	$2.5 \times 10^2$	$5.3 \times 10^4$	*	—

\*Electrical conductivity was lost.

The above procedure was repeated in the same manner as described above except that the palladium chloride was replaced with silver nitrate, silver sulphate, gold chloride and platinum chloride, respectively, whereby an improvement in washability was attained in each resultant textile.

#### Example 12

A copper sulphide-carrying, electrically conducting fibre, obtained in the same manner as described in Example 1 of United States patent No. 4,336,028 except that the concentrations of cupric sulphate, sodium thiosulphate and sodium hydrogen sulphite were each reduced in half, was immersed in an aqueous silver nitrate solution having different concentrations and treated at a temperature of 50°C for 2 hours to obtain seven kinds of electrically conducting fibres with different atomic ratios Ag/Cu as shown in Table 2. Each sample was subjected to the washability test with the results shown in Table 2.

TABLE 2

Ag/Cu atomic ratio	Number of washing operation			
	0	10	30	50
	Electrical resistivity ( $\Omega$ -cm)			
0	$1.16 \times 10^{-1}$	$1.65 \times 10^{-1}$	$3.86 \times 10^6$	*
0.0005	$1.14 \times 10^{-1}$	$1.21 \times 10^{-1}$	$2.6 \times 10^2$	$5.8 \times 10^5$
0.0011	$1.27 \times 10^{-1}$	$1.26 \times 10^{-1}$	$1.8 \times 10^{-1}$	$4.2 \times 10^{-1}$
0.013	$1.29 \times 10^{-1}$	$1.30 \times 10^{-1}$	$1.36 \times 10^{-1}$	$1.9 \times 10^{-1}$
0.16	$2.14 \times 10^{-1}$	$2.12 \times 10^{-1}$	$2.21 \times 10^{-1}$	$2.6 \times 10^{-1}$
0.31	$3.6 \times 10^1$	$3.6 \times 10^1$	$3.5 \times 10^1$	$3.7 \times 10^1$
0.42	$6.36 \times 10^3$	$6.40 \times 10^3$	$6.28 \times 10^3$	$6.5 \times 10^3$

\*Electrical conductivity was lost.

#### Claims

1. An electrically conducting material comprising a cyano group-containing material having adsorbed thereby sulphides of copper and at least one auxiliary metal selected from the group consisting of silver, gold and elements of the platinum group.

2. An electrically conducting material as claimed in claim 1, wherein said cyano group-containing material is a synthetic polymeric material or a natural polymer material having introduced therein cyano groups.

3. An electrically conducting material as claimed in claim 2, wherein said synthetic polymeric material includes an acrylonitrile polymer or copolymer.

4. An electrically conducting material as claimed in claim 2, wherein said synthetic polymeric material includes a synthetic polymeric substance having introduced therein cyano groups.

5. An electrically conducting material as claimed in claim 2, wherein said natural polymeric material includes a polypeptide or a polysaccharide.

6. An electrically conducting material as claimed in claim 1, wherein said cyano group-containing material includes a water-insoluble low molecular compound having one or more cyano groups.

7. An electrically conducting material as claimed in any of claims 1 to 6, wherein said cyano group-containing material is in the form of powder or a shaped body.

8. An electrically conducting material as claimed in any of claims 1 to 7, wherein the amount of the sulphide of copper is about 0.5 to 30% in terms of elemental copper based on the weight of the cyano group-containing material.

9. An electrically conducting material as claimed in claim 8, wherein the amount of the sulphide of the auxiliary metal is such that the atomic ratio M/Cu, where M stands for the auxiliary metal, is in the range of about 0.0001 to 0.5.

10. An electrically conducting material as claimed in claim 9, wherein the atomic ratio M/Cu is in the range of about 0.001 to 0.3.

11. An electrically conducting material as claimed in any of claims 1 to 10, wherein the auxiliary metal is silver.

12. An electrically conducting material as claimed in any of claims 1 to 11, further comprising the sulphide of iron, cobalt or nickel adsorbed on the cyanic group-containing material.

13. A process for the preparation of an electrically conducting material, comprising treating a cyano group-containing material with (a) a source of monovalent copper ions, (b) a source of ions containing an auxiliary metal selected from the group consisting of silver, gold and elements of the platinum group and (c) a sulphur-containing compound to adsorb sulphides of copper and the auxiliary metal by the cyano group-containing material.

14. A process as claimed in claim 13, wherein the treatment with component (a) is simultaneous with the treatment with component (b) and prior to the treatment with component (c).

15. A process as claimed in claim 13, wherein the treatment with component (b) is simultaneous with the treatment with component (c) and is separate from and subsequent to the treatment with component (a).

16. A process as claimed in claim 13, wherein the treatment with components (a), (b) and (c) is within the same treating bath.

17. A process as claimed in any of claims 13 to 16, wherein said source of monovalent copper ions includes a copper compound and a reducing agent capable of reducing bivalent copper ions into monovalent copper ions.

18. A process as claimed in claim 17, wherein said reducing agent is selected from the group consisting of metallic copper, hydroxylamine, a salt of hydroxylamine, ferrous sulphate, ammonium vanadate, furfural, sodium hypophosphite, glucose and mixtures thereof.

19. A process as claimed in any of claims 13 to 18, wherein said sulphur-containing compound is selected from the group consisting of sodium sulphide, sulphur dioxide, sodium hydrogen sulphite, sodium pyrosulphite, sulphurous acid, dithionous acid, sodium dithionite, sodium thiosulphate, thiourea dioxide, hydrogen sulphide, sodium formaldehyde sulphonylate, zinc formaldehyde sulphonylate and mixtures thereof.

20. A method of improving the stability of an electrically conducting, copper sulphide-carrying, cyano group-containing material, comprising treating said cyano group-containing material with a source of ions containing an auxiliary metal selected from the group consisting of silver, gold and elements of the platinum group, to adsorb a sulphide of the auxiliary metal by the cyano group-containing material.

21. A method as claimed in claim 20, wherein said treatment is conducted in the presence of a sulphur-containing compound.

22. A method as claimed in claim 20, further comprising treating the product of said treatment with a sulphur-containing compound.

23. A method as claimed in claim 21 or 22, wherein said sulphur-containing compound is selected from the group consisting of sodium sulphide, sulphur dioxide, sodium hydrogen sulphite, sodium pyrosulphite, sulphurous acid, dithionous acid, sodium dithionite, sodium thiosulphate, thiourea dioxide, hydrogen sulphide, sodium formaldehyde sulphonylate, zinc formaldehyde sulphonylate and mixtures thereof.

#### Patentansprüche

1. Elektrisch leitendes Material, gekennzeichnet durch einen die Zyangruppe enthaltenden Stoff unter Adsorption von Kupfersulfiden und zumindest einem Zusatzmetall aus der Gruppe Silber, Gold und Elementen der Platingruppe.

2. Elektrisch leitendes Material nach Anspruch 1, dadurch gekennzeichnet, daß ein synthetisch oder natürlich vorkommender polymerer Stoff mit eingebrachten Zyangruppen als zyangruppenhaltiger Stoff verwendet wird.

3. Elektrisch leitendes Material nach Anspruch 2, dadurch gekennzeichnet, daß der synthetisch polymere Stoff ein Akrylnitril-Polymer oder Copolymer umfaßt.

4. Elektrisch leitendes Material nach Anspruch 2, dadurch gekennzeichnet, daß der synthetisch polymere Stoff eine synthetisch polymere Substanz umfaßt, in die Zyangruppen eingebracht sind.



5. Elektrisch leitendes Material nach Anspruch 2, dadurch gekennzeichnet, daß der natürlich vorkommende polymere Stoff Polypeptid oder Polysaccharid umfaßt.

6. Elektrisch leitendes Material nach Anspruch 1, dadurch gekennzeichnet, daß der zyangruppenhaltige Stoff eine wasserlösliche niedermolekulare Verbindung mit einer oder mehreren Zyangruppen umfaßt.

5 7. Elektrisch leitendes Material nach einem der vorhergehenden Ansprüche 1 bis 6, dadurch gekennzeichnet, daß der zyangruppenhaltige Stoff in Form von Pulver oder als Formkörper verwendet wird.

8. Elektrisch leitendes Material nach einem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß der Anteil an Kupfersulfid in Form von elementarem Kupfer auf der Basis dem Gewichts des zyangruppenhaltigen Stoffes etwa 0,5 bis 30% beträgt.

10 9. Elektrisch leitendes Material nach Anspruch 8, dadurch gekennzeichnet, daß der Sulfidanteil des Zusatzmetalls derart bemessen ist, daß das Atomverhältnis M/Cu, wobei mit M das Zusatzmetall gemeint ist, etwa im Bereich von 0,0001 bis 0,5 liegt.

10. Elektrisch leitendes Material nach Anspruch 9, dadurch gekennzeichnet, daß das Atomverhältnis M/Cu etwa im Bereich von 0,001 bis 0,3 liegt.

11. Elektrisch leitendes Material nach einem der vorhergehenden Ansprüche 1 bis 10, dadurch gekennzeichnet, daß als Zusatzmetall Silber verwendet wird.

12. Elektrisch leitendes Material nach einem der vorhergehenden Ansprüche 1 bis 11, gekennzeichnet darüber hinaus durch am zyangruppenhaltigen Stoff adsorbiertes Eisen-, Kobalt- oder Nickelsulfid.

13. Verfahren zum Herstellen eines elektrisch leitenden Materials, gekennzeichnet durch Behandeln eines zyangruppenhaltigen Stoffes mit (a) einem monovalenten Kupferionen-Lieferanten, (b) einem Ionen-Lieferanten, der ein der Silber- und Goldgruppe sowie den Elementen der Platingruppe zugehöriges Zusatzmetall enthält, und (c) mit einer schwefelhaltigen Verbindung, so daß vom zyangruppenhaltigen Stoff Kupfersulfide und das Zusatzmetall adsorbiert werden.

14. Verfahren nach Anspruch 13, dadurch gekennzeichnet, daß der Behandlungsschritt (a) gleichzeitig mit dem Behandlungsschritt (b) und vor dem Behandlungsschritt (c) durchgeführt wird.

15. Verfahren nach Anspruch 13, dadurch gekennzeichnet, daß der Behandlungsschritt (b) gleichzeitig mit dem Behandlungsschritt (c) und getrennt sowie nachfolgend auf den Behandlungsschritt (a) durchgeführt wird.

16. Verfahren nach Anspruch 13, dadurch gekennzeichnet, daß die Behandlungsschritte (a), (b) und (c) im selben Behandlungsbad durchgeführt werden.

17. Verfahren nach einem der vorhergehenden Ansprüche 13 bis 16, daß der monovalente Kupferionen-Lieferant eine Kupferverbindung sowie ein Reduktionsmittel umfaßt, durch das zweiwertige Kupferionen zu einwertigen Kupferionen reduziert werden.

18. Verfahren nach Anspruch 17, dadurch gekennzeichnet, daß das Reduktionsmittel gewählt wird aus einer Gruppe, die metallisches Kupfer, Hydroxylamin, Hydroxylaminsalz, Eisen(II)-sulfat, Trioxovanadat(V), Furfural, Natriumhypophosphit, Glukose und Gemenge aus diesen umfaßt.

19. Verfahren nach einem der vorhergehenden Ansprüche 13 bis 18, dadurch gekennzeichnet, daß die schwefelhaltige Verbindung gewählt wird aus der Gruppe, die Natriumsulfid, Schwefeldioxid, Natriumhydrogensulfid, Natriumpyrosulfid, schwefelige Säure, Dithionsäure, Natriumdithionit, Natriumthiosulfat, Thioharnstoffdioxid, Hydrogensulfid, Natriumformaldehydsulfoxylat, Zinkformaldehydsulfoxylat und Gemenge aus diesen umfaßt.

20. Verfahren zur Stabilitätsverbesserung eines elektrisch leitenden, Kupfersulfid tragenden und zyangruppenhaltigen Materials, gekennzeichnet durch Behandeln des zyangruppenhaltigen Stoffes mit einem Ionen-Lieferanten, der ein Zusatzmetall enthält, das gewählt ist aus einer Gruppe, die Silber, Gold und Elemente der Platingruppe umfaßt, so daß vom zyangruppenhaltigen Stoff ein Sulfid des Zusatzmetalls absorbiert wird.

21. Verfahren nach Anspruch 20, dadurch gekennzeichnet, daß die Behandlung in Anwesenheit einer schwefelhaltigen Verbindung durchgeführt wird.

22. Verfahren nach Anspruch 20, dadurch gekennzeichnet, daß der Verfahrensschritt darin besteht, daß das Erzeugnis der Behandlung mit einer schwefelhaltigen Verbindung behandelt wird.

23. Verfahren nach einem der vorhergehenden Ansprüche 21 oder 22, dadurch gekennzeichnet, daß die schwefelhaltige Verbindung gewählt wird aus der Gruppe, die Natriumsulfid, Schwefeldioxid, Natriumhydrogensulfid, Natriumpyrosulfid, schwefelige Säure, Dithiosäure, Natriumdithionit, Natriumthiosulfat, Thioharnstoffdioxid, Hydrogensulfid, Natriumformaldehydsulfoxylat, Zinkformaldehydsulfoxylat und Gemenge aus diesen umfaßt.

## Revendications

1. Matériau conducteur de l'électricité, comprenant un matériau contenant un groupe cyano ayant, sous forme adsorbée de ce fait, des sulfures de cuivre et d'au moins un métal auxiliaire choisi dans le groupe formé de l'argent, de l'or et des éléments du groupe du platine.

2. Matériau conducteur de l'électricité selon la revendication 1, dans lequel le matériau contenant un groupe cyano est un matériau polymère synthétique ou un matériau polymère naturel dans lequel des groupes cyano ont été introduits.

3. Matériau conducteur de l'électricité selon la revendication 2, dans lequel le matériau polymère synthétique contient un polymère ou copolymère d'acrylonitrile.

4. Matériau conducteur de l'électricité selon la revendication 2, dans lequel le matériau polymère synthétique contient une substance polymère synthétique dans laquelle des groupes cyano ont été introduits.

5. Matériau conducteur de l'électricité selon la revendication 2, dans lequel le matériau polymère naturel contient un polypeptide ou un polysaccharide.

6. Matériau conducteur de l'électricité selon la revendication 1, dans lequel le matériau contenant un groupe cyano contient un composé insoluble dans l'eau et de faible masse moléculaire, ayant 1 ou plusieurs groupes cyano.

7. Matériau conducteur de l'électricité selon l'une quelconque des revendications 1 à 6, dans lequel le matériau contenant un groupe cyano est sous forme d'une poudre ou d'un corps conformé.

8. Matériau conducteur de l'électricité selon l'une quelconque des revendications 1 à 7, dans lequel la quantité de sulfure de cuivre est d'environ 0,5 à 30% de cuivre élémentaire par rapport au poids du matériau contenant un groupe cyano.

9. Matériau conducteur de l'électricité selon la revendication 8, dans lequel la quantité du sulfure du métal auxiliaire est telle que le rapport atomique M/Cu, M désignant le métal auxiliaire, est compris entre environ 0,0001 et 0,5.

10. Matériau conducteur de l'électricité selon la revendication 9, dans lequel le rapport atomique M/Cu est compris entre environ 0,001 et 0,3.

11. Matériau conducteur de l'électricité selon l'une quelconque des revendications 1 à 10, dans lequel le métal auxiliaire est l'argent.

12. Matériau conducteur d'électricité selon l'une quelconque des revendications 1 à 11, comprenant en outre le sulfure de fer, de cobalt ou de nickel adsorbé sur le matériau contenant un groupe cyano.

13. Procédé de préparation d'un matériau conducteur de l'électricité, comprenant le traitement d'un matériau contenant un groupe cyano par (a) une source d'ions cuivre monovalents, (b) une source d'ions contenant un métal auxiliaire choisi dans le groupe formé par l'argent, l'or et les éléments du groupe du platine, et (c) un composé contenant du soufre, afin que des sulfures de cuivre et du métal auxiliaire soient adsorbés par le matériau contenant un groupe cyano.

14. Procédé selon la revendication 13, dans lequel le traitement par le constituant (a) est simultané au traitement par le constituant (b) et antérieur au traitement par le constituant (c).

15. Procédé selon la revendication 13, dans lequel le traitement par le constituant (b) est simultané au traitement par le constituant (c) et est séparé du traitement par le constituant (a) et postérieur à ce dernier traitement.

16. Procédé selon la revendication 13, dans lequel le traitement par les constituants (a), (b) et (c) est effectué dans le même bain de traitement.

17. Procédé selon l'une quelconque des revendications 13 à 16, dans lequel la source d'ions cuivre monovalents contient un composé du cuivre et un agent réducteur capable de réduire des ions cuivre bivalents en ions cuivre monovalents.

18. Procédé selon la revendication 17, dans lequel l'agent réducteur est choisi dans le groupe qui comprend le cuivre métallique, l'hydroxylamine, un sel de l'hydroxylamine, le sulfate ferreux, le vanadate d'ammonium, le furfural l'hypophosphite de sodium, le glucose et leurs mélanges.

19. Procédé selon l'une quelconque des revendications 13 à 18, dans lequel le composé contenant du soufre est choisi dans le groupe formé par le sulfure de sodium, l'anhydride sulfureux, le sulfite acide de sodium, le pyrosulfite de sodium, l'acide sulfureux, l'acide dithionieux, le dithionite de sodium, le thiosulfate de sodium, le bioxyde de thiourée, l'hydrogène sulfuré, le formaldéhyde sulfoxyolate de sodium, le formaldéhyde sulfoxyolate de zinc et leurs mélanges.

20. Procédé d'augmentation de la stabilité d'un matériau contenant un groupe cyano, portant du sulfure de cuivre et conducteur de l'électricité, comprenant le traitement du matériau contenant un groupe cyano par une source d'ions contenant un métal auxiliaire choisi dans le groupe qui comprend l'argent, l'or et les éléments du groupe du platine, afin qu'un sulfure du métal auxiliaire soit adsorbé par le matériau contenant le groupe cyano.

21. Procédé selon la revendication 20, dans lequel le traitement est réalisé en présence d'un composé contenant du soufre.

22. Procédé selon la revendication 20, comprenant en outre le traitement du produit du traitement par un composé contenant du soufre.

23. Procédé selon l'une des revendications 21 et 22, dans lequel le composé contenant du soufre est choisi dans le groupe qui comprend le sulfure de sodium, l'anhydride sulfureux, le sulfite acide de sodium, le pyrosulfite de sodium, l'acide sulfureux, l'acide dithionieux, le dithionite de sodium, le thiosulfate de sodium, le bioxyde de thiourée, l'hydrogène sulfuré, le formaldéhyde sulfoxyolate de sodium, le formaldéhyde sulfoxyolate de zinc et leurs mélanges.